SCRATCH CELL TEST- a simple, cost effective screening tool to evaluate self - healing in anti corrosion coatings

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Abstract

A quick and simple scratch cell set up was fabricated to evaluate the self - healing in a room temperature cured,methacrylate anti-corrosion hybrid sol-gel coating on aerospace aluminium alloy AA2024-T3, with minimum instrumentation. The inhibitors Cerium nitrate, Benzotriazole and 8-hydroxy quinoline (8-HQ) were used in the study. The decreasing self-healing ability of the inhibitors was in the following order 8HQ, BTZ and Ce. 8-HQ showed the best self - healing effect and was comparable to the commercial hexavalent chromium conversion coating – Alodine. Spectroscopic analysis of the electrolyte and EDX of the coatings indicated the movement of the inhibitor from the coating, thereby effecting self - healing. Increased inhibitor concentration in the coatings did not hasten the healing process. Compared to inhibitor spiked coatings, coatings doped with inhibitor loaded nano-containers indicated slower release of the inhibitor, a property desirable in self - healing coatings. Electro impedance studies further confirmed self-healing.

The scratch cell study reported here is the first of its kind with the ormosil under study on AA2024-T3 aluminium alloy. The results are encouraging and warranty a quick and simple semi - qualitative screening of the self - healing potential of the inhibitors with minimum instrumentation.

Keywords: Scratch cell, inhibitors, cerium nitrate, 8HQ, benzotriazole, self-healing.

1. Introduction

Aluminium alloys 2XXX, 6XXX and 7XXX series have a wide range of applications in automobile, aerospace and marine industry. AA2024-T3 is susceptible to localized pitting corrosion due to the presence of secondary phase particles such as copper inter-metallics

promoting galvanic activity [1]. In view of the ban on use of hexavalent chromium in anti-corrosion coatings, search for alternate anti-corrosion coatings for aerospace applications is ongoing. Of late, organic-inorganic hybrid sol -gel coatings have attracted interest as suitable replacement to chromate conversion coatings (CCC) due to their green nature and ease of fabrication [2-5]. The method involves hydrolysis and condensation of silicon alkoxides to produce a 3-dimensional, amorphous, porous and stable silica network the sol- gel ormosil coating is believed to act as a passive/barrier [6-9]. However, passive barrier coatings are not practically viable in any engineering sector, especially in the aerospace sector as they could require frequent replacements of aircraft structures due to inadvertent coating damage or scratches.

One of the ways to provide active protection to metals is to introduce corrosion inhibitors in the coatings. In the event of damage to the coating, the inhibitors are released from the coating, thus imparting “self-healing” to the coatings [9-11]. Hence, as the aircraft/machinery downtime costs are expensive, “smart coatings” with “self- healing" abilities would be an ideal choice.

Self-healing is a relatively new and rapidly growing concept in materials science, wherein, upon external or internal damage of the coating, repair occurs from the damage-related environment itself without the aid of any external factors [12-14].

Thus, in the present study, a room temperature cured methacrylate based ormosil coating, doped with inhibitors was evaluated for its anti-corrosion and self-healing property [15, 16]. Methacryloxypropyl trimethoxy silane (MEMO), was used as the continuous phase i.e., matrix, Tetraethyl orthosilane (TEOS), as the non-hydrolysable organic binder, Triethoxy vinylsilane (VTEOS) as the discontinuous phase organic precursor i.e., filler and nitric acid as catalyst. The inhibitors-8-HQ, Benzotriazole and Cerium nitrate were evaluated in the present study (Fig.1).

A plethora of inhibitors and their derivatives have been reported to offer protection against corrosion[17] and it would be a marathon task to evaluate all of them. A quick and simple test method, without compromising on the quality of results and confirming to the test standards, would help immensely in screening the self - healing ability of several corrosion inhibitors, thus saving time and resources. A few rapid test methods for corrosion analysis, choice of inhibitors have been reported by some group [18-21]. Muster *et al* (2009)[17] have reported a multi-electrode method, while Chambers *et al* (2007)[18] developed a luminescent

based method, However, the authors have adapted routine electrochemical tests for corrosion analysis, which is time consuming and requires specalised equipment.

We report here a simple scratch cell set up, through which self- healing ability of a large number of coatings can be initially screened by simple optical microscopy and subsequently, the coatings, indicating self-healing can be subjected to detailed analysis through routine electrochemical tests. This will help save time and resources. The primary focus of the study is the first layer of the coating system, i.e. conversion coating (surface pre-treatment step).

EXPERIMENTAL PROCEDURE

Materials

The precursor silanes, Tetra ethyl ortho silane (TEOS, 98%), Methacryloxy propyl trimethoxy silane (MEMO, 98%) and Vinyltriethoxy silane (VTEOS, 98%) were purchased from Gelest, USA and used as received. 30% Ludox silica (12 nm), Polyethyleneimine (PEI), (MW-60,000) and Polystyrene sulphonate (PSS) (MW-70,000), Cerium(III) nitrate hexahydrate, benzotriazole and 8-hydroxy quinoline were procured from Sigma Aldrich. Millipore Milli-Q water with resistance of 18.2MΩ was used for dilutions and reagent preparation. All other solvents and chemical were purchased locally. AA-2024 - T3 aluminium alloy coupons (25 x15 x 1.2 mm) were used as substrate and the composition of the alloy is shown in Table1.

Element	Al	Cu	Mg	Zn	Fe	Mn	Cr	Ni	Si
2024-T3	93.52	4.24	1.26	0.08	0.15	0.65	<0.01	ND	0.06

Table 1 Composition of the substrate AA 2024-T3

Surface pre- treatment

The surface of the test coupons was degreased with acetone followed by chemical etching, wherein the samples were dipped in an alkaline aqueous solution for 4 minutes at 60^{o}C, followed by 2 minutes dip in nitric acid and finally in NaOH solution. The samples were rinsed in Milli - Q water after each step.

Preparation of polyelectrolyte (PE) solutions

Aqueous solutions of PEI and PSS (1%) were prepared using autoclaved Milli-Q water to prevent microbial contamination. The pH of the PE solutions was adjusted to pH 6.0 with suitable acid/base.

Preparation of colloidal Ludox silica nano-containers

Colloidal silica-PE nano-containers were prepared by the method of Shchukin *et al* (2006)[21]. A known volume of colloidal silica (15 wt%) in Milli-Q water was stirred alternatively with a definite volume of PEI /PSS solution for 15 mins at 25ºC.After the required number of layers,the nano-containers from the solution were pelleted by centrifugation at 1000 rpm for 5 mins, and subsequently washed three times with Milli-Q water, by centrifugation. These nano-containers comprised of the following layers (SiO_2/PEI/PSS/PEI/PSS/PEI) and will be referred to as *undoped nano-containers*.

The inhibitor doped nano-containers were prepared with inhibitor layer sandwiched between the PSS layer and comprised of the following layers (SiO_2/PEI/PSS/inhibitor/PSS/inhibitor/PEI**)**. The bound inhibitor concentration of the nano-containers was back calculated from the unbound inhibitor in the washes, analysed by spectroscopy. The undoped and doped nano-containers were stored at 8°C until further use.

Preparation of Ormosil coating (C1)

The ormosil comprising of TEOS, MEMO and VTEOS was prepared as described by Metroke *et al* (2004)[15]. Hydrolysis and condensation was initiated by addition of 0.05N HNO_3, and stirred for 1h at 25ºC in a closed reactor. The water was supplied by the catalyst solution for complete hydrolysis and condensation through formation of Si-O-Si bonds. The resultant sol was diluted with equal volume of ethanol and used immediately. Two millilitres of this mixture was sprayed on fresh chemically etched AA-2024 coupons, and clean glass slides.

Preparation of Ormosil coatings spiked with inhibitor (C2)

An appropriate quantity of inhibitor (500ppm) was added directly to the sol, prepared as described above, stirred well and sonicated for 3h for uniform dispersal of the inhibitor. A known volume of this mixture was sprayed on fresh chemically etched AA-2024 coupons and clean glass slides.

Preparation of Ormosil coatings with doped nano-containers (C3)

A pre-determined quantity of undoped/inhibitor doped nano-containers and ormosil were mixed, diluted with ethanol, and sonicated for one hour, to obtain the desired concentrations of inhibitor (500 and 1500 ppm). A fixed volume of this mixture was then sprayed on fresh chemically etched AA-2024 coupons and clean glass slides. The coatings fabricated with each inhibitor were as follows.

(i) Ormosil - C1

(ii) Ormosil +inhibitor spiked (500ppm) - C2

(iii) Ormosil +inhibitor doped (500ppm, 1500 ppm) - C3

A higher concentration (1500ppm) was premeditatedly used in the doped coatings to ensure release of sufficient inhibitor for self-healing, and rule out false negative results due to insufficient levels of inhibitor. At lower concentrations, enough inhibitor may not be released from the nano-container for effective self-healing.

Chromate conversion coating with commercial Alodine was used as a positive control to understand self-healing, as observed under an optical microscope.

The coatings were aged for a minimum of 7 days at 25^{o}C before surface analysis and self-healing evaluation. A scribe (area of 400mm^2) was made in the centre of the coupon using an automatic template scribber (Fig.2) to maintain uniformity in depth and width of the scribe, and reduce false positive results. It is reported that the scribe width determines self – healing [22].

Characterization and evaluation

Surface Characterisation: The morphology of the coatings was evaluated using the optical microscope (Vertical Metallurgical Microscope attached to a camera) at 50X and 100X periodically at 0, 6, 12, 24, 48, .188h (7days). Surface changes (peeling, discoloration etc) on the panels particularly the scribed region was visually monitored periodically, and at the end of the stipulated time, visualised under FE-SEM, Carl Zeiss Supra 40. The elemental analysis of the coating/scribed region was performed by EDAX.

On completion of stipulated time periods, panels were taken out; ultra sonicated for 20 mins in distilled water, and observed using optical microscopy. The coating thickness was measured using a 2D profilometer, while the coating hardness on the coupons was determined

using Elcometer 501, Pencil Hardness Tester (ASTM D3363-92a). The leaching rate of the inhibitors into the electrolyte was studied using UV-VIS Spectrometer, Perkin Elmer Instruments, Lambda 35. The λ max of the inhibitor was calculated by performing a scan in the UV- VIS region. A standard calibration curve was plotted and the concentration of the inhibitor in the electrolyte, calculated from the respective standard curves.

Self- healing property

Scratch Cell Set Up

A scratch cell arrangement was used to study self-healing in the silane based coatings. Alodine coating was used as a positive control to monitor and compare the self-healing ability of the present coating under study with respect to the Chromium conversion coating. The cell arrangement was meant to duplicate a mechanical defect scratch in a coating and also to understand the movement or release of the inhibitor to enabling repair or self - healing of the damaged silane film loaded with inhibitors. The arrangement (Fig.3) consisted of 2 panels sandwiching a neoprene rubber O-ring of diameter 1.5 cms and 0.2 cms thickness containing 0.5 ml of 3.5% NaCl as the electrolyte [20].The electrolyte acted as a bridge, between the lower and upper coupon, enabling the movement of the inhibitor from the lower coupon to the top coupon. In all the tests, only the lower or bottom coupon had a coating with inhibitor, while the top coupon was coated with ormosil alone minus the inhibitor.

The cell set up was dismantled at regular intervals (0, 6,12,24,48...188h) to (i) monitor the leaching and movement of the inhibitor from the bottom coupon coating to the top coupon via the electrolyte (ii) self-healing of the scribed region and (iii) ensure the presence of electrolyte, The volume of the electrolyte was measured and made up to the original volume of 0.5ml.

RESULTS AND DISCUSSION

The studies indicated that all the bottom coupons (with inhibitor) revealed varying degrees of self-healing (Fig.4). The coating thickness ranged from 1-2 μm and hardness 4B-F.The observed self-healing was almost comparable to the self-healing seen with hexavalent chromate coatings, which was used as a positive control.

In the chromate conversion coatings, both top and bottom coupons showed self-healing. Interestingly, although self - healing was observed in both the top and bottom

coupons (Fig.4b) of CCC, Cr was not detectable in the top coupon by EDX analysis (Table 2).

Coatings with 8-HQ

Self-healing was best in coatings loaded with 8-HQ followed by benzotriazole and Cerium. Self-healing was observed in both spiked (within 24h) and in doped coatings (by 188h). (Fig. 5). As expected, self - healing was not observed in coatings doped with lower concentration of the inhibitor (500pppm), probably due to the low/sub-optimal release of the inhibitor for effective self-healing.Sself-healing was not observed in the bare coupons and coatings with ormosil alone.

The self-healing observed visually in the optical pictures is supported by EDX analysis of the coatings (Table 2). The presence of nitrogen in the EDX analysis is indicative of the inhibitor (8-HQ) [23]. The coatings showed the presence of carbon and aluminum suggesting thin coatings. Higher concentrations of oxygen (24 wt %) observed in the doped coatings as compared to as prepared coatings are indicative of self-healing.(data not shown). During corrosion, there is massive consumption of oxygen, but when self-healing occurs, the demand for oxygen decreases from the cathodic areas and oxygen is able to act partially as a mediator in the feedback mode, thus there is an accumulation of oxygen on the coatings[24].

Spectroscopic estimation of the inhibitor concentration in the electrolyte indicated that less than 10% of the inhibitor had leached out into the electrolyte (Table 3) and was sufficient to initiate self – healing. However, it is opined that higher concentrations of the inhibitor may hasten the process, especially in the doped coatings.

Wt%	CCC top	CCC bottom	8HQ spiked bottom (500ppm)	Benzo doped bottom (1500ppm)	Benzo doped top (1500ppm)	Ce Spiked bottom (500ppm)
C	17.43	14.91	14.81	15.84	18.26	14.76
O	52.63	30.04	47.38	49.73	41.07	53.54
Mg	0.52	0.58	0.55	0.83	0.53	0.53
Al	26.96	38.07	32.50	25.91	24.36	27.60
Si	0.48	0.50	1.85	5.82	8.44	3.57
Ce	-	-	-	-	-	**1.13**
N	-	-	**1.21**	**1.88**	**0.80**	-
Cu	1.99	1.92	2.91	-	1.36	1.83
Cr	**-**	**13.97**	-	-	-	-

Table 2: EDX analysis of the coatings

Sl.no	Coating	Inhibitor Concentration ppm (from calibration graph)		
		8HQ	**Benzotriazole**	**Cerium**
1	**Spiked 500ppm**	38.20	28.22	25.67
2.	**Doped 500ppm**	5.55	9.95	14.75
3.	**Doped 1500ppm**	21.9	26.14	32.31

Table 3: Spectroscopic analysis of the electrolyte after 188h .

Electrochemical impedance studies : The self healing property in coating C3 is further corroborated by the electro chemical impedance studies (Fig.6.). Higher impedance value denotes better protection. Doped coating C3 at low frequency of 0.01Hz had an impedance value of 10^6 Ω-cm^2,remained almost constant even after 168h of immersion in 3.5%NaCl. While in C2, the undoped coating although the initial impedance was high, it dropped nearly 500 times on immersion for 168h in the electrolyte ..This clearly indicates the corrosion protection by self – healing offered by the inhibitor in the coating.

Coatings with Benzotriazole

Benzotriazole spiked coatings (500ppm) also showed self - healing from 24h and healing improved with immersion time, the maximum tested time period of 188h (Fig 7). In

coatings with higher doping concentration of benzotriazole (1500 ppm), both the bottom and top coatings revealed the presence of the inhibitor (nitrogen) (Table 2, Fig.8).

As can be observed from Table.2, the concentraion of nitrogen was almost double in the bottom coupon (1.88) compared to the top coupon (0.80), indicative of the possible movement of the inhibitor from the bottom doped coupon to the undoped top coupon through the electrolyte. The inhibitor had to be from the bottom coating as the top coatings did not contain the inhibitor.

In addition, the absence of Cu can be noted in the bottom coupon with (Table 2) benzotriazole, indicating the probable formation of Cu-BTZ complex, the mechanism by which Benzotriazole is believed to protect the alloy AA2024- T3 [20] .

Coatings with Cerium

Self-healing was observed in both spiked and doped coatings. The EDX analysis of the coatings spiked with cerium revealed the presence of Ce, thereby confirming the movement of the inhibitor from the coating into the scribed region, as is expected in the self - healing mechanism (Table 2 and Fig. 9). Cerium was detected (1.12 wt %) outside the scribed region (Fig.10).

Spectroscopic analysis of the electroyte to study the movement of the inhibitor from the bottom to the top coupon, indicated the presence of the inhibitor in the electrolyte,(Table 3), as determined from the standard graph.

Self - healing was also observed in coatings, doped with higher concentration of Cerium nitrate (1500 ppm) after 48h of immersion (Fig 10a,b). Self-healing took place in the bottom coupon, but not in the top coupon, indicating that, in case of Ce, doping with 1500 ppm was insufficient to cause self- healing and higher concentrations were required. This could be due to the fact that the inhibitor is lodged inside the nano container released in smaller quantities may be insufficient to bring about effective self-healing.However, self-healing was observed in the Ce spiked (500ppm) samples as the inhibitor was readily available for healing. Corrosion protection at 6000 ppm of Cerium has been reported [25].

Conclusions: The scratch cell test to evaluate self-healing in ormosil coatings was performed with three inhibitors namely, 8-HQ, Benzotriazole and cerium nitrate. The results indicated self-healing with 8-HQ to be the best and comparable to the CCC coating, used as a positive

control. The findings are supported by EIS, EDX analysis and FE-SEM. The scratch cell method is a quick, semi-qualitative, high throughput method to evaluate self-healing with minimum instrumentation.

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Figure Legends

Fig. 1. (a) Cerium (III) nitrate (b) Benzotriazole (c) 8-Hydoxy quinoline.

Fig.2. Coated coupon showing the scribe

Fig.3. Schematic representation of scratch cell test set up

Fig. 4. FE-SEM of the (a) bottom coupons (b) chromium conversion coated coupons (magnification- 300X)

Fig.5. Optical microscopy of bottom coupons with 8- HQ from the scratch cell set up

Fig.6 .Bode and Nyquist plots for coating C3 after 168h of immersion.

Fig. 7: Optical microscopy of Benzotriazole spiked-bottom (500ppm)

Fig. 8. FESEM showing self - healing in (a) top and (b) bottom coupon doped with benzotriazole
(1500 ppm).Magnification -300X

Fig. 9. Optical microscopy of Ce spiked bottom (500ppm)

Fig.10. FE –SEM showing the presence of Ce in the coating

Fig.10. Optical microscopy of the Ce doped-(a) bottom (b) top (1500ppm)